

TECHNICAL REPORT

NO. 9

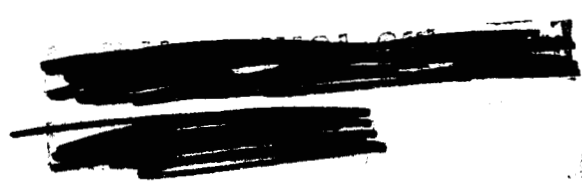
THE ABSOLUTE ENERGY OF THE  $A^3\Sigma_u^+$   
STATE OF NITROGEN

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NASA RESEARCH GRANT  
NsG 193-62

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
Washington, D. C.



### Foreward

This report is a manuscript of a paper which has been submitted for publication in the Journal of Molecular Spectroscopy. The experiment described herein is part of a continuing series of laboratory work in support of our upper atmospheric program.

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## 1. Introduction

The absolute energy of the  $A^3\Sigma_u^+$  state of molecular nitrogen is of importance since this fixes the relative energy between the singlet and triplet states. This state is the upper level of the forbidden Vegard-Kaplan system and the lower level of the intense First Positive system.

The 0-4, 0-5, and 0-6 bands of the Vegard-Kaplan system have been obtained previously with very high resolution<sup>1</sup> and values for these band origins are given in Table I.

In order to make use of these Vegard-Kaplan bands for determining the energy of the  $A^3\Sigma$  state, it is necessary to know the energy values for the  $v = 4, 5$ , and  $6$  vibrational levels of the  $X^1\Sigma_g^+$  ground state. These can be obtained from the more intense Lyman-Birge-Hopfield system. However, the wavenumbers for the bands required for determining the energy of these vibrational levels were either not yet determined or known with an accuracy of 100 times less than those of the Vegard-Kaplan bands.<sup>2</sup> We therefore undertook a high resolution analysis of the L-B-H bands.

## 2. Experimental

All of the spectra used for our analysis were obtained with the five-meter two-mirror spectrograph described previously.<sup>3</sup> The  $5 \times 10$  inch, 300 grooves per mm grating used for this work is blazed at  $5.9\mu$  in the first order and thus all the L-B-H bands were obtained at high orders. For example, the  $1415\text{\AA}$  (1-0) band was taken in the 41st order, with a resolving power limited by the Doppler width of the lines, and a reciprocal dispersion of about  $0.07 \text{\AA}$  per mm ( $3.6 \text{ cm}^{-1}$  per mm). Tests on the use of overlapping orders with this grating have shown no coincidence errors for wavelengths in the visible and

near ultraviolet regions. However, we have not yet determined this for the vacuum ultraviolet region so that there may be a very slight shift in the wavenumbers given in this paper. Overlapping orders were avoided by means of a grating cross-disperser which employed a 3 600 grooves per mm plane grating.

The wavelength reference source used for all exposures was the iron hollow cathode discharge tube.<sup>4</sup> Its use with this spectrograph has been described previously.<sup>1</sup>

The plate measurements were reduced with the aid of a computer program which consisted of a least squares fit to the grating equation appropriate for this spectrograph.

The discharge tube consisted of a  $\frac{1}{4}$  inch I. D. pyrex glass tube about 10 inches long. The tube was surrounded by a water jacket and large air-cooled electrodes were situated at both ends. The window was made of lithium fluoride. A pressure of about 0.5 mm of Hg and a current of 200 milliamperes was found to give the strongest emission. The exposure times varied from 10 to 30 hours using Kodak SWR photographic plates.

### 3. Results

A detailed analysis of the L-B-H bands will be given elsewhere. Here we need only the band origins, and these can be obtained using the wavenumbers of the lines of the intense Q branch and the formula

$$Q(J) = \nu_0 + (B' - B'')J(J + 1) - (D' - D'')J^2(J + 1)^2$$

Using this method we have obtained precise band origins for 10 selected bands. They are given in Table II together with previously published values.

From the L-B-H band origins the ground state vibrational

levels for  $v = 4, 5$ , and  $6$  are found to be

$$\begin{aligned}\Delta G_{4-0} &= 9\,147.54\text{ cm}^{-1} \\ \Delta G_{5-0} &= 11\,362.61 \\ \Delta G_{6-0} &= 13\,548.72\end{aligned}$$

Combining these with the Vegard-Kaplan band origins, a term value of  $49\,754.78\text{ cm}^{-1}$  was obtained for the  $A^3\Sigma_u^+$  ( $v = 0, J = 0$ ) state relative to the  $X^1\Sigma_g^+$  ( $v = 0, J = 0$ ) ground state. The possible error should be less than  $0.02\text{ cm}^{-1}$ . This value is a refinement of  $1.12\text{ cm}^{-1}$  of the value  $49\,755.90\text{ cm}^{-1}$  obtained by Dieke and Heath.<sup>6</sup> The latter value was obtained by combining the results of their analysis of the First Positive system with the results of Wilkinson's<sup>7</sup> unresolved absorption spectrum of the 6-0 and 7-0 Vegard-Kaplan bands.

Our value can be added to the energy values given by Dieke and Heath<sup>6</sup> in their Table 5 in order to obtain the energy values for the rotational and vibrational structure of the  $A^3\Sigma$  state.

One can also obtain the energy values for the  $A^3\Sigma$  state without recourse to the band origins. One merely adds or subtracts the proper wave numbers, obtained from the wavelength measurements, so as to determine the energy values of the individual rotational levels for all the states involved. We have done this and found the results to be in excellent agreement with the term value given above.

#### Acknowledgements

The author is grateful to the late Professor G. H. Dieke for his advice and assistance in this work; to Dr. H. M. Crosswhite for his help with the computer program and wavelength standards and for reading the manuscript.

This work was carried out under a grant to The Johns Hopkins University from the National Aeronautics and Space Administration (Grant NsG 193-62).

Table I

Band Origins for Three V-K Bands

Band	$\nu_o$
0 - 4	$40\,607.246 \pm 0.003 \text{ cm}^{-1}$
0 - 5	$38\,392.167 \quad 0.003$
0 - 6	$36\,206.048 \quad 0.002$

Table II  
Band Origins of the L-B-H Bands

$v' - v''$	$\nu_o$ (cm <sup>-1</sup> )	$\nu_o$ (cm <sup>-1</sup> )
0-0	68 951.24	68 951.21 ( <u>2</u> )
0-4	59 803.71	58 803.48 ( <u>5</u> )
0-5	57 588.64	
0-6	55 402.53	
1-0	70 617.58	70 617.58 ( <u>2</u> )
1-4	61 470.02	
1-5	59 254.97	59 254.55 ( <u>5</u> )
1-6	57 068.85	
2-0	72 256.08	72 256.16 ( <u>2</u> )
2-6	58 707.35	

The values in column three are those obtained by Wilkinson and Houk (5) and Wilkinson (2).

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